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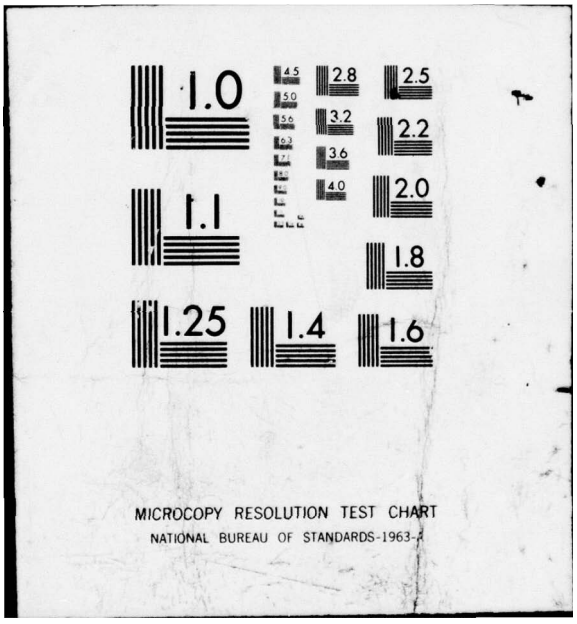
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INDEXING THE DEGREE OF HYDROGEN EMBRITTLEMENT OF 4340 STEEL USING THE BARNACLE ELECTRODE.

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NAVAL AIR DEVELOPMENT CENTER
Warminster, Pennsylvania 18974

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3 NOVEMBER 1976

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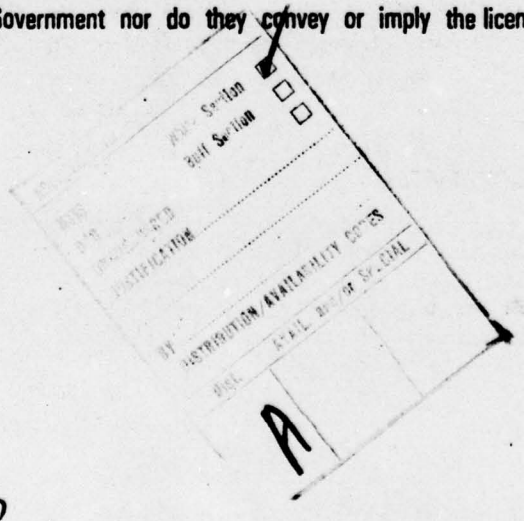

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The barnacle electrode, an electrochemical device based on the hydrogen permeation method, was used, in conjunction with sustained load tests, to index the degree of embrittlement of 4340 steel. Flat, double notched tensile specimens of 250 ksi (1725 MPa) notched tensile strength and having a K_t of 5.6 were shown to have a critical diffusible hydrogen concentration of 1.9, 1.7, 1.4, 1.2, 0.9 and 0.5 ppm for loads of 15, 20, 25, 30, 35 and 40 percent of the notched tensile strength.

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SUMMARY

INTRODUCTION

The phenomenon of hydrogen entering high strength steels, such as the landing gear of Naval aircraft, causing catastrophic failure when under stress is a well known problem. It is important, therefore, to know the hydrogen concentrations that a part can contain without failing at service loads, and to be able to measure this hydrogen. In the course of development experiments with the barnacle electrode system, an electrochemical device for the in situ measurement of embrittling mobile hydrogen in high strength steels, it was found that a critical hydrogen concentration for cracking of 4340 steel appeared to exist at given stress levels. Therefore, this study was undertaken to index the degree of embrittlement in this alloy over a range of stresses, as well as to determine critical concentrations. This project was authorized by the Naval Air Systems Command and was carried out as part of the ongoing research on corrosion and corrosion resistant materials, AIRTASK No. R 0220 101, Work Unit No. DG 202.

SUMMARY OF RESULTS

Flat, double notched tensile specimens of AISI 4340 steel of 250 ksi (1725 MPa) notched tensile strength and having a K_t of 5.6 were shown to have critical diffusible hydrogen concentrations of 1.9, 1.7, 1.4, 1.2, 0.9 and 0.5 ppm for sustained loads of 15, 20, 25, 30, 35 and 40 percent of the notched tensile strength (NTS).

CONCLUSIONS

It was shown that it is possible to index the degree of hydrogen embrittlement of a high strength steel with the barnacle electrode; that hydrogen concentrations as low as 0.5 ppm can be determined; that these low levels of hydrogen can be embrittling; and that the barnacle electrode measuring time can be reduced from thirty to twenty minutes.

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It is well known that hydrogen can enter high strength steels in many ways causing a loss in ductility which may result in catastrophic failure. This hydrogen can exist in a very low concentration in the steel and yet cause damage because the hydrogen in a metal under stress migrates to areas of high stress intensity, magnifying its effect (references (a), (b) and (c)).

The barnacle electrode is being developed by the Aeronautical Materials Laboratory as a device intended for the in situ measurement of embrittling mobile hydrogen in high strength steel parts. The principle of the barnacle electrode is based on the electrochemical coulometric method of hydrogen permeation and is described elsewhere (references (d) and (e)).

In the course of laboratory experiments with the barnacle electrode system, it was found that a critical concentration for mobile hydrogen to cause cracking of 4340 steel appeared to exist for the stress level used (reference (d)). It therefore seemed advisable to investigate this system more fully in order to index the degree of embrittlement over a range of stresses, as well as to confirm the existence of this critical concentration.

Devanathan and Stachurski (references (f) and (g)) were the first to use a very sensitive electrochemical technique to measure the rate of permeation of hydrogen through thin metal membranes. This method requires that a diffusion gradient exist within the metal foil by producing hydrogen on one side, e.g., by cathodic charging, and removing it on the other side by anodic polarization with a potentiostat. By keeping the exit surface at zero hydrogen concentration in this manner, the oxidizing current is, therefore, a direct indication (through Faraday's law) of the rate of diffusion of hydrogen. Analysis of the build-up and decay transients can then be used to give diffusivity/concentration information (references (d), (e) and (h)).

The barnacle electrode technique makes use of only the anodic side of the permeation cell. A nickel/nickel oxide electrode replaces the potentiostat to create and maintain the potential to extract and oxidize the hydrogen (which is uniformly distributed throughout the specimen) and thus maintain zero hydrogen concentration at the exit surface of the specimen. The boundary conditions are thus established for solution of the diffusion equations (references (d) and (h)). The first term Laplace transform solution according to Gileadi (reference (h)) is given by equation (1)

$$C_o = \frac{J}{ZF} \left(\frac{\pi t}{D} \right)^{\frac{1}{2}} \qquad (1)$$

where C_o = concentration of hydrogen — mol cm^{-3}

J = oxidation current density — A cm^{-2}

F = Faraday — 96500 C mol^{-1}

Z = number of electrons in oxidation reaction

t = time — s

D = diffusivity — cm^2 s^{-1}

If the experimental extraction current-time transient fits the curves calculated from the above equation, and if the diffusivity of hydrogen through the given steel is known, a measurement of J for any given time will give the hydrogen content, C_o.

The degree of embrittlement is a function, not only of the hydrogen concentration, but also of the material, including its heat treatment and its geometry which determines the stress concentration factor, K_t. It is, therefore, necessary to do mechanical testing and correlate failure data with the electrochemical measurements for the material of interest.

EXPERIMENTAL PROCEDURES

The specimens used in this study were double notched, 0.063 inch (1.60 mm) thick tensile bars of AISI 4340 steel having a notched tensile strength of 250 ksi (1725 MPa) and a K_t of 5.6. They were finished by surface grinding, then swabbed with 2 percent aqueous HCl in methanol, rinsed with methanol, and wiped with a Kimwipe just prior to charging.

Hydrogen was introduced by cathodic charging of the entire specimen for three hours at a constant current in a solution containing one percent each of NaOH and NaCN, the latter acting as a poison to promote hydrogen uptake (reference (i)). The charging rate (i.e., current density) was varied to provide different hydrogen levels. The anode was a cylindrical platinum gauze surrounding the specimen.

After charging, the specimen was rinsed with de-ionized water followed by a methanol rinse and dried with a Kimwipe. The barnacle electrode was then assembled and measurements taken within 15 minutes of charging using 0.2 M NaOH as electrolyte.

After the thirty-minute barnacle measurement, the specimen was rinsed with water and dried, then stressed in a constant load stress rupture machine. Specimens still intact after one week were considered unembrittled. Failure usually occurred within one-half hour. Thus, a fail-no fail criterion was established.

The barnacle cell consists of a hollow Teflon block which has a 1.0 cm^2 circular opening which fits against the specimen. The contact surface is a raised rim of approximately 4 mm diameter which provides a pressure fit when the clamp is tightened. As extra assurance for a sharp, reproducible solution contact area, a replaceable, 0.1 mm thick Teflon gasket is glued to this rim with rubber cement. The cell is clamped to the specimen with a special C-clamp which has a thumbscrew for tightening. The nickel/nickel oxide electrode is a piece of nickel/cadmium battery positive plate having a nickel contact strip.

The complete setup is shown pictorially and schematically in Figures 1 and 2, respectively.

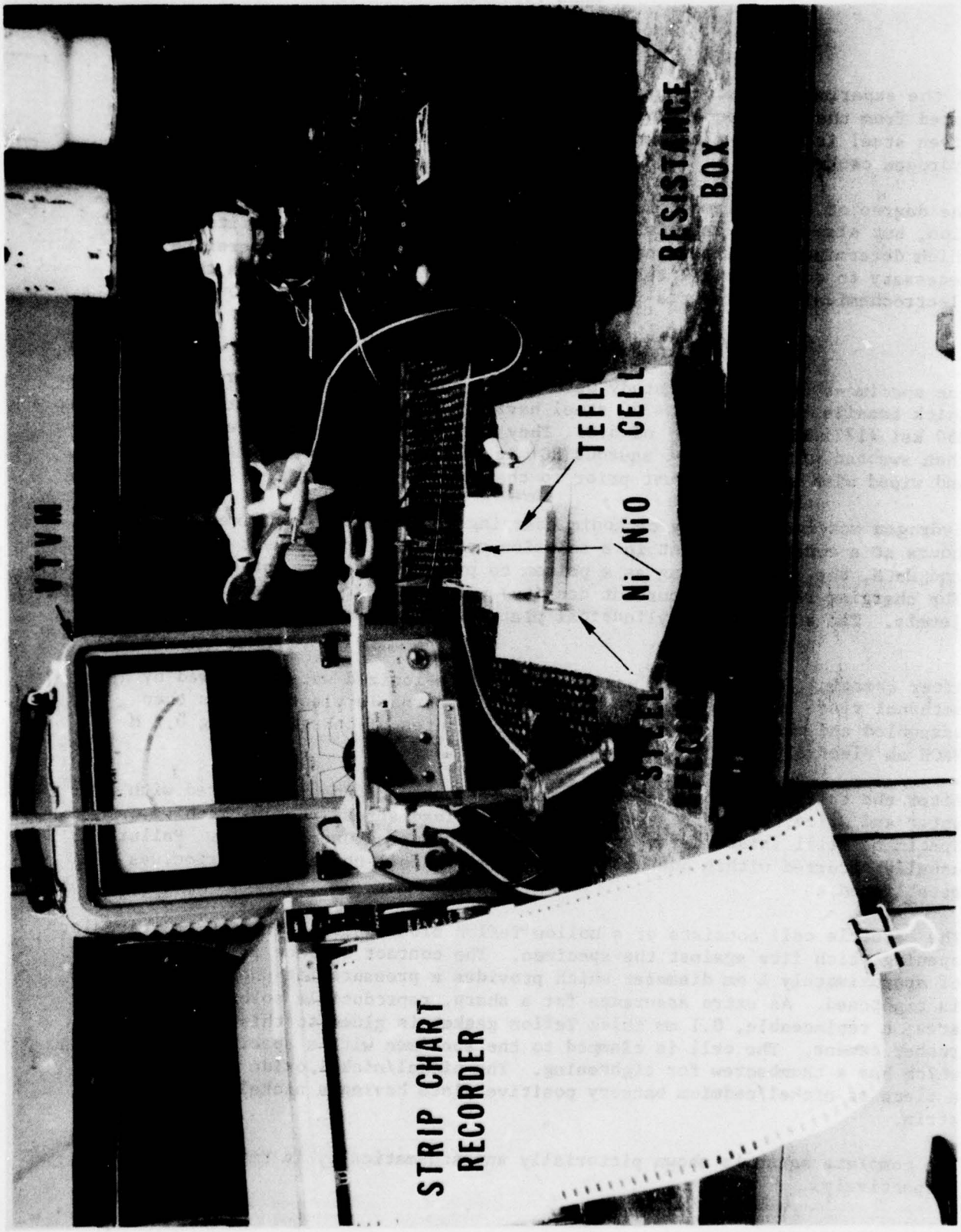

Figure 1. Barnacle Electrode Measuring Apparatus

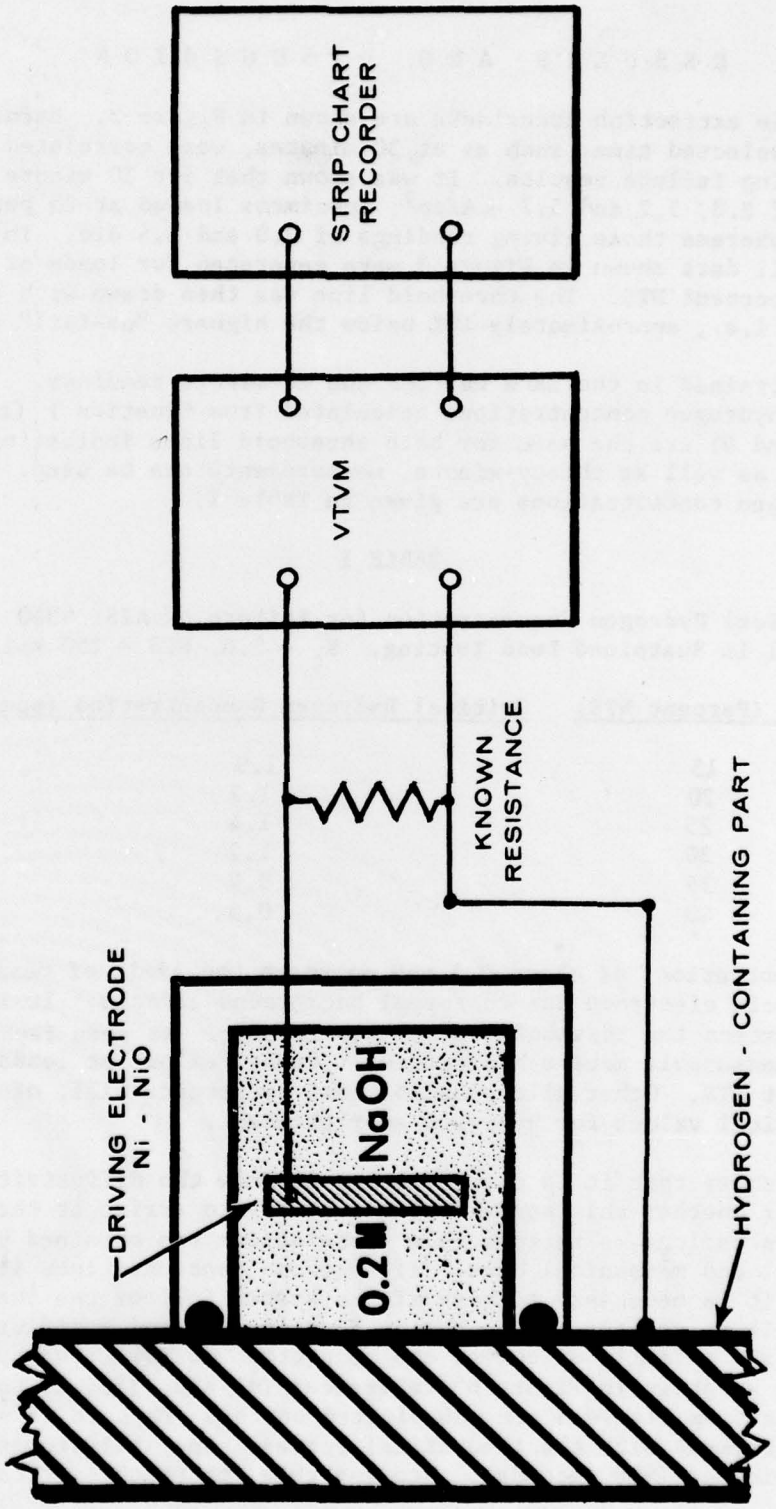

Figure 2. Schematic of Barnacle Electrode Measuring Apparatus

RESULTS AND DISCUSSION

Typical barnacle extraction transients are shown in Figure 3. Barnacle readings at a selected time, such as at 30 minutes, were correlated with sustained loading failure results. It was shown that for 30-minute barnacle measurements of 2.8, 5.2 and 5.7 $\mu A/cm^2$, specimens loaded at 25 percent NTS did not fail, whereas those giving readings of 7.0 and 7.4 did. In this way, the fail-no fail data shown in Figure 3 were generated for loads of 15, 20, 25, 30 and 40 percent NTS. The threshold line was then drawn with a 10 percent safety factor; i.e., approximately 10% below the highest "no-fail" points.

Figure 4 was obtained in the same way for the 20-minute readings. It can be seen that the hydrogen concentrations calculated from Equation 1 (right hand axes in Figures 4 and 5) are the same for both threshold lines indicating that twenty-minute, as well as thirty-minute, measurements can be used. These critical hydrogen concentrations are given in Table I.

TABLE I

Critical Hydrogen Concentration for Failure of AISI 4340 Steel in Sustained Load Testing. $K_t = 5.6$, NTS = 250 ksi

Load (Percent NTS)	Critical Hydrogen Concentration (ppm)
15	1.9
20	1.7
25	1.4
30	1.2
35	0.9
40	0.5

Hydrogen concentrations of about 0.5 ppm approach the limit of measurement with the barnacle electrode due to normal background effects. It is unnecessary to extend the threshold curves any further. As seen from Figures 4 and 5, any measurable mobile hydrogen will cause failure at loads greater than 40 percent NTS. Other alloys and/or heat treatments will, of course, give different critical values for hydrogen embrittlement.

The foregoing shows that it is not necessary to know the diffusivity of hydrogen in the steel or whether this system follows theory to arrive at threshold barnacle values as long as reproducible correlations are obtained between the electrochemical and mechanical data. If hydrogen concentrations are desired, however, then it is necessary to know if the system follows the theoretical equation (Eq. 1) at various times. Using Equation (1) and a diffusivity of 2.5×10^{-7} $cm^2 s^{-1}$ a family of curves can be plotted for selected hydrogen concentrations as shown in Figure 6 (references (d) and (j)). If the extraction transients from Figure 3 are now plotted on this graph it is seen that they are in good agreement with the theoretical curves, especially for times in excess of 15 minutes (900 seconds). Knowing this, these theoretical curves

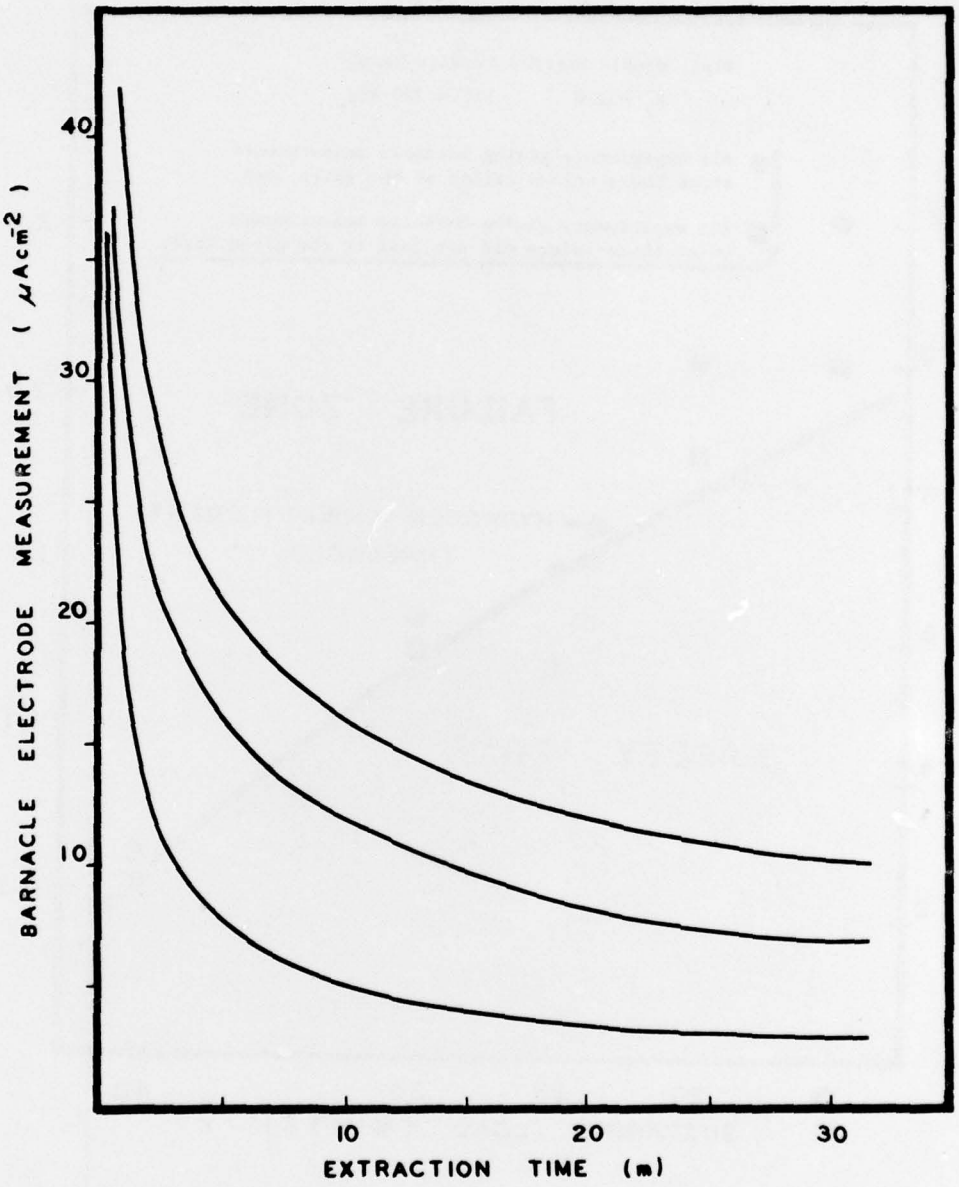

Figure 3. Typical Barnacle Electrode Hydrogen Extraction Transients

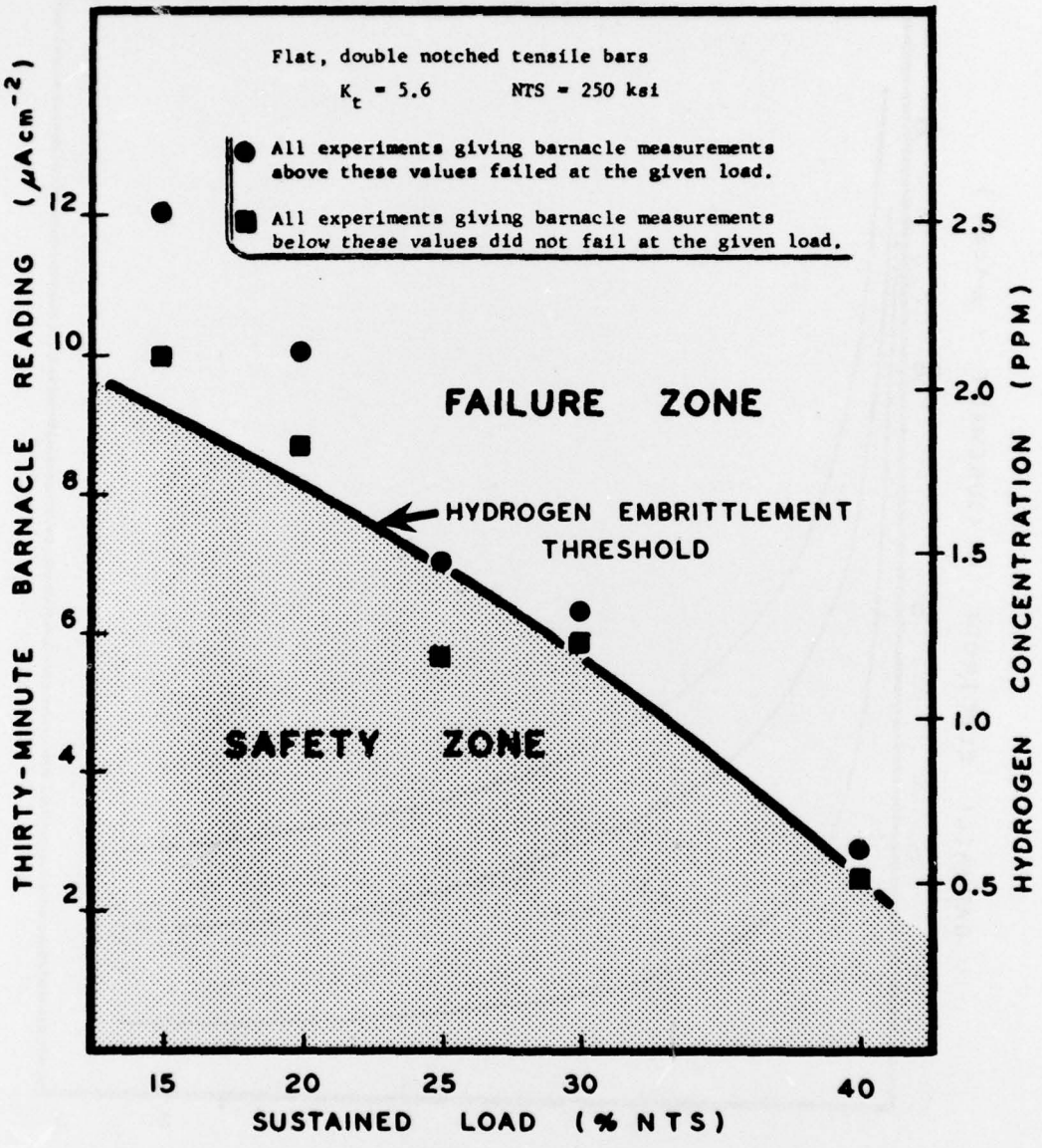

Figure 4. Indexing the Degree of Hydrogen Embrittlement of AISI 4340 Steel Using Thirty-Minute Barnacle Electrode Measurements.

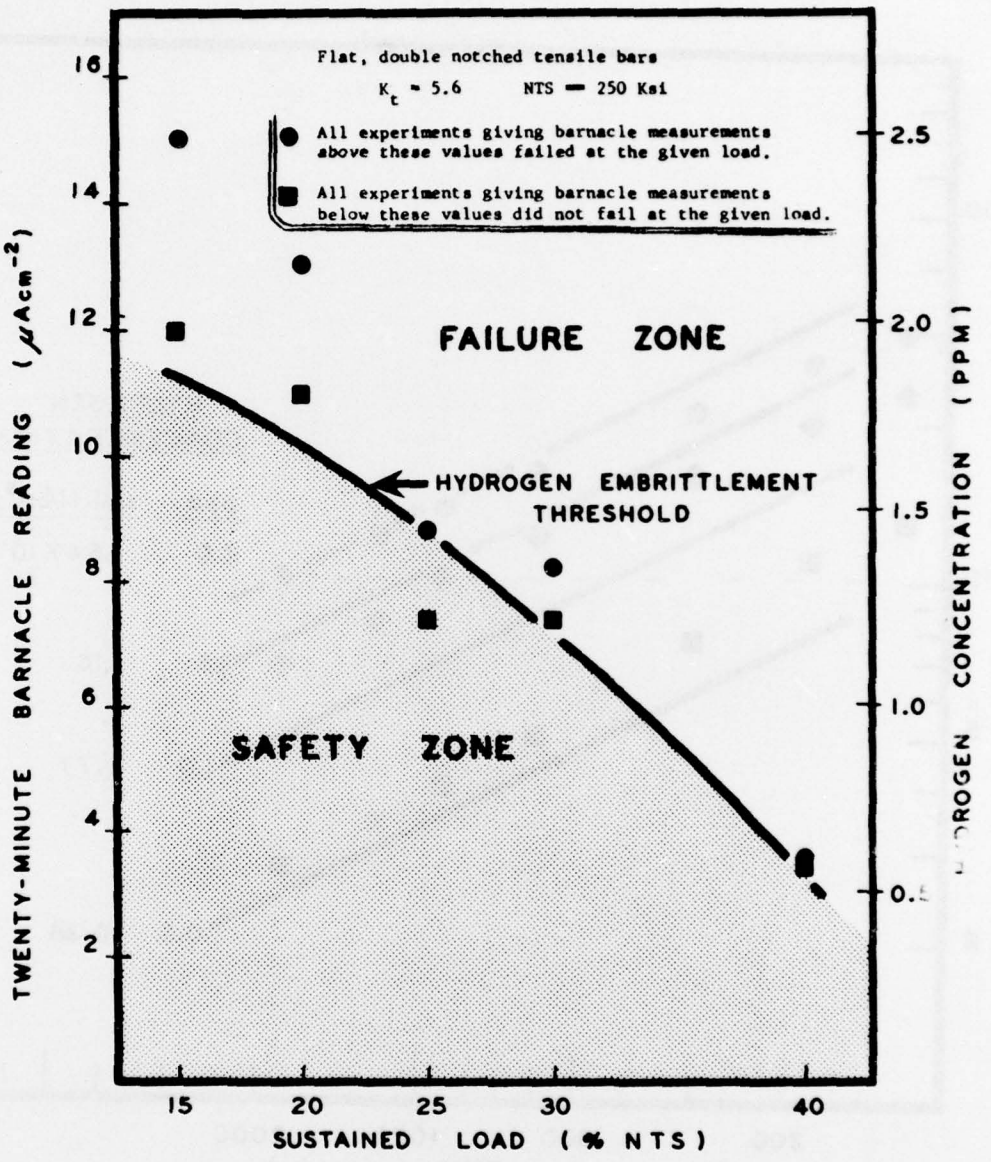

Figure 5. Indexing the Degree of Hydrogen Embrittlement of AISI 4340 Steel Using Twenty-Minute Barnacle Electrode Measurements.

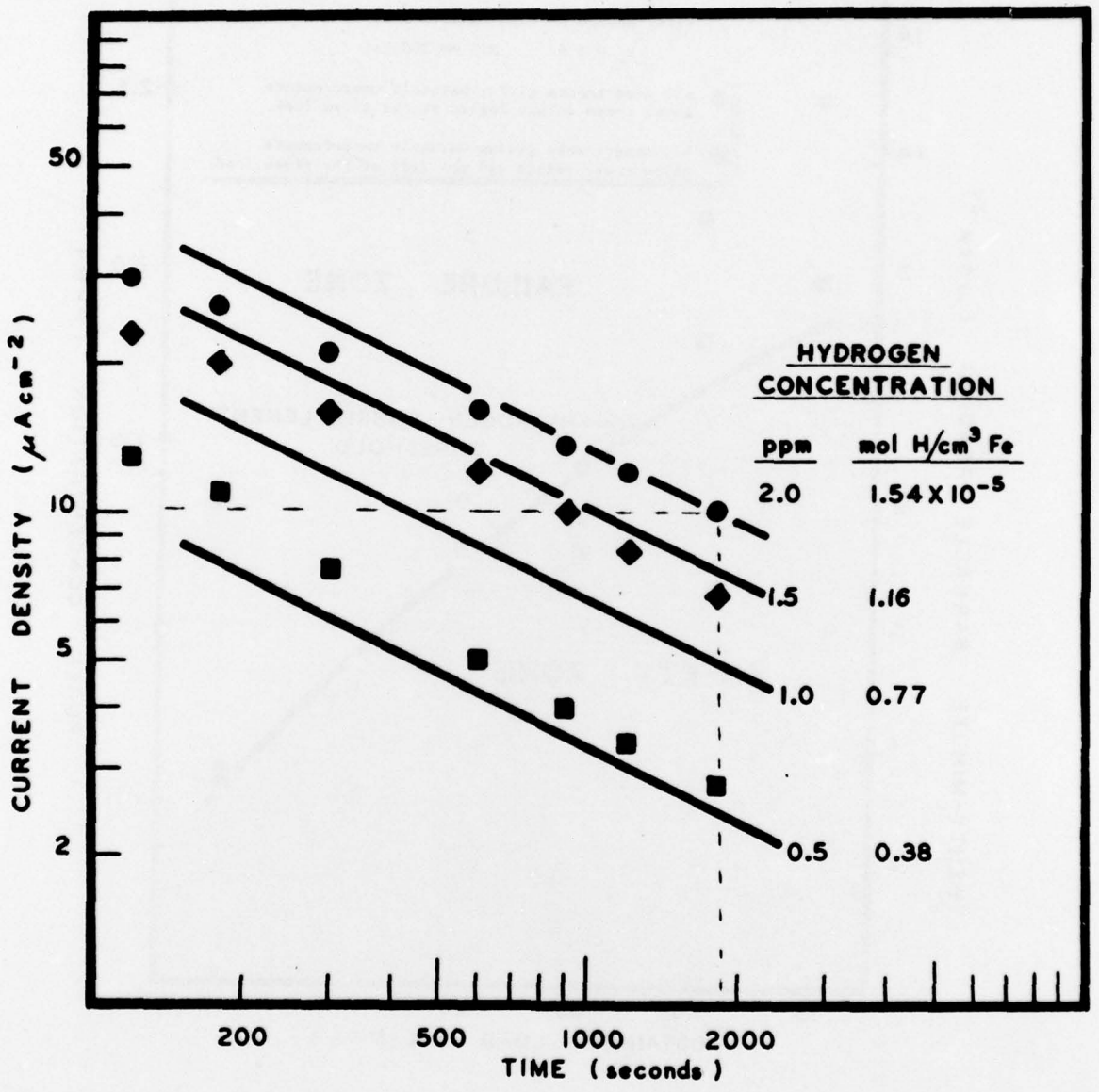

Figure 6. Barnacle Electrode Hydrogen Extraction Transients vs Theoretical Curves Calculated from Equation (1) for AISI 4340 Steel, D = 2.5 x 10^{-7} cm^2s^{-1}.

can be used in conjunction with a barnacle reading to determine the mobile hydrogen concentrations. Taking a 30-minute barnacle reading of 10 $\mu A/cm^2$, for example, it is seen by the dotted lines in Figure 6 that the hydrogen concentration is 1.5×10^{-5} mol/cm^3 (2.0 ppm).

Alternatively, hydrogen concentrations can be calculated using Equation (1). Table II shows the results of these calculations for all of the specimens used in this study at selected extraction times. Concentrations are given in parts per million (1 mol $H/cm^3 = 1.3 \times 10^5$ ppm). It can be seen that the calculated concentrations agree for each specimen from 15 to 30 minutes indicating agreement with the theoretical equation.

TABLE II

Calculated Hydrogen Concentrations (ppm) from Barnacle Electrode Measurements at Selected Extraction Times.

Specimen No.	5	10	15	20	30 min.
1	1.1	1.5	1.0	1.0	.99
2	1.6	2.3	1.7	1.6	1.6
3	1.6	2.5	1.7	1.8	1.7
4	1.7	2.7	1.9	2.0	2.0
5	---	3.5	2.4	2.5	2.4
6	1.7	2.5	1.9	1.8	1.8
7	1.9	2.8	2.0	2.1	2.0
8	.63	.85	.57	.56	.57
9	.99	1.5	1.0	1.0	1.1
10	1.2	1.8	1.3	1.2	1.2
11	1.4	2.0	1.4	1.5	1.4
12	1.2	1.8	1.4	1.5	1.5
13	1.4	2.0	1.3	1.2	1.2
14	1.3	2.0	1.4	1.4	1.4
15	1.5	2.2	1.4	1.4	1.3
16	.77	.95	.61	.56	.51
17	.58	.82	.57	.58	.59
18	.99	1.6	1.1	1.1	1.0
19	.52	.65	.44	.43	.45

CONCLUSIONS

This study confirmed preliminary results that the barnacle electrode could be used to index the degree of hydrogen embrittlement of a high strength steel, and that reproducible results, which fit the theoretical equation, could be obtained. By using flat, double notched tensile specimens of AISI 4340 steel having a notched tensile strength of 250 ksi (1725 MPa) and a K_t of 5.6, critical hydrogen concentrations for failure of 1.9, 1.7, 1.4, 1.2, 0.9 and 0.5 ppm were found for sustained loads of 15, 20, 25, 30, 35 and 40 percent of the NTS, respectively. It was shown that hydrogen concentrations as low as 0.5 ppm can be determined, and that these low levels of hydrogen can be embrittling. It was further shown that twenty-minute measurements are as suitable as those taken at thirty minutes.

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